

GLYCEROL AND
SPENT LYE CLARIFICATION

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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GLYCEROL and SPENT LYE CLARIFICATION

A THESIS

Presented by

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To the

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Preface.

In selecting a thesis I have tried to keep in mind the uppermost object of a technical training, a training that should enhance, not ones⁷ routine powers, but ones² powers of worldly insight and commercial attack.

A technical graduate should be likened to a casting of untold dimensions, ready for the process of polishing, rather than an atomical dot already finished over by the routine grind.

With the time that I have at my disposal I deem it advisable to select some small problem connected with the industrial laboratory or the like.

Hence with the sentiments as set forth above I have selected a phase of soap lye clarification, a rapid analysis of glycerol by carbon dioxide evolution and a brief compilation of data and literature.

R. D. P., 1915.

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Introduction.

In the general advance of technical knowledge and research during the last century the soap industry has not remained stationary. About 1823 Chevreul published his researches on the constitution of fats, showing that instead of consisting of a single substance they were composed of fatty acids in combination with a base, glycerol, and that glycerol was contained in the waste liquors of the soap and candle factories.

When the remarkable properties of glycerol, such as its permanence and non-volatility at ordinary temperatures, its softening effects on the skin and the value in cosmetic preparations, its oily nature combined with its miscibility with water and alcohol, its enormous solvent powers, its sweet and agreeable taste and finally its value as a base for the most valuable of all explosives, nitroglycerine and dynamite, which are not known in any other one substance, became known manufacturers began to

figure how this soap lye, which had been run off into the gutters, might be worked for its valuable glycerine content.

Soap lye as run from the kettle, consists of water, holding in solution the salt added to separate the soap, in the form of sodium hydrate and carbonate, albuminous matter and free alkali, both in solution and suspension, in certain cases gums, and the glycerol.

The problem that confronted and still confronts the soap and glycerine manufacturer is how to get this valuable glycerol out of that conglomeration and into a pure state in the easiest and cheapest manner.

Glycerol, as it is produced, amounts to 85,000 tons annually. The glycerine industry is exclusively a by-product industry of the soap and candle trade and the output depends not so much on the demand for glycerine as on the worlds requirements of soap and candles.

This condition is brought about by the fact that fats only contain from 10.5 %

glycerol in tallow to 13.5 % in cocoanut oil. In practice this percentage of glycerol is cut down by the free fatty acids in the fat, each 10 % of free fatty acids in the fats reducing the percentage of glycerol by about 10 %.

(Rogers.)

Glycerol has been subject to wide fluctuations in price; the "dynamite" grade selling at 10 cents per pound in 1908, 26 cents per pound in 1911, and 18 cents per pound in 1915. The United States does not produce enough glycerol for its own use hence from 30 to 40 million pounds of foreign crude are imported annually.

Lye Clarification.

Glycerol is so closely associated with the soap industry that no soap plant is complete without its department for saving the glycerol contained in the fats and oils used by the soap maker.

For many years chemists and engineers have been directing their energies toward improving processes and machinery for the recovery of glycerol from spent soap lye. Many patents have been granted and many processes developed each having a common object of glycerol recovery. There can be traced a gradual evolution in efficiency of procedure and apparatus designed to remove the organic matter from the lye, to concentrate this clarified lye, thereby removing the greater part of the dissolved salts, and to continue the concentration till crude glycerine is obtained, which further remains to be purified by distillation.

Metallic salts, such as sulphate of iron and aluminum, were used in the early stages of lye treatment for coagulating and purifying agents, as in the process of L. M. Brochon, in 1882 and J. P. Battershall in 1883 and later by Van Ruymbeke in 1891. The Van Ruymbeke process for recovering the glycerol from still fats was an important step in 1894. In 1904 Garrigue developed his process for eliminating volatile fatty acids previous to distillation.

Domeir and Hagemann, in 1890 first used the closed salt separator which was later applied to vacuum evaporators by Foster in 1899. O. Laist, in 1893 applied the air condenser to glycerol stills, but the first use of vacuum had been in 1882 in connection with the apparatus of Armandy. In 1891 Van Ruymbeke combined the use of the high vacuum with heating still by means of saturated steam; in 1894 applied the injection of expanded and reheated steam to glycerine stills.

In 1904 Garrigue utilized the heat of the glycerine vapor for superheating low pressure steam injected into the still. (For a complete account of the distillation and refining of crude glycerine the reader is referred to the literature.)

Spent soap lyes as produced by the modern soap factory vary in quality depending upon the practice of the soap maker. The refiner would of course prefer to receive lyes free from impurities and coloring matter, but the object of passing water through the kettle is to remove the dirt and coloring matter from the soap as well as to obtain a good yield of glycerol. It is advisable, however, to avoid running nigre and rosin lye to the glycerine plant, and this can only be done when the glycerine has been properly removed from the soap before the nigre and rosin are added.

The yield of glycerine obtainable from soap stock is entirely dependent on the amount

of the lye removed from the kettle. The best practice is to get about 90 % of the glycerine in the stock into the crude. To obtain this yield necessitates the removal of at least three pounds of lye per pound of stock saponified, not counting any rosin that may have been used.

If rosin and nigre lyes are used there will be much coloring matter from the rosin and nigre. All lyes will separate some soap on cooling and a storage tank should be provided for the lye waiting to be heated and from which the separated soap can be skimmed. No lyes should be drawn from the glycerine tanks in the plant containing sufficient strength to raise the average of all the lyes to more than 0.4 % total alkalinity. This low figure will result in a large saving both in caustic soda in the soap factory and acid used to neutralize the alkalinity of the lye in the glycerine plant.

After the soap has cooled and all the

separated soap has been skimmed off it is removed to the glycerine plant where it is to be treated before going to the evaporators. The alkali in the lye must be neutralized and the organic impurities removed.

The neutralization of the alkali is affected by the addition of hydrochloric or sulphuric acids. The use of the former is open to objection due to high cost. It has the advantage, however, of producing as a result of the chemical action, sodium chloride which after recovery can be used again in the soap kettle.

Sulphuric acid is most generally used. Its use introduces sulphate into the lye which salt is recovered with the common salt from the evaporator. Sodium sulphate however is practically useless for graining soap, its graining qualities being but three fifths that of sodium chloride and the grain produced is soft and often hard to separate from the lye.

To remove the organic impurities some

means must be employed to render them insoluble. This is best accomplished by the addition of metallic salts, forming insoluble metallic compounds, which are coagulated when the lye is neutralized.

The chief aim in using a metallic salt in the purification of soap lyes is the removal of the soaps of the lower fatty acids, formic, acetic, butyric, caprylic, etc.,.

The amount of aluminum sulphate to be used depends on the cleanliness of the lye and its freedom from soap and gelatinous matters. The least amount that will give a good cake in the filter press and not gum the cloths is the amount to use. This salt can be added either dry or dissolved in water and will neutralize about one third its weight of caustic soda. An excess of caustic soda in the lye has the tendency to form aluminum hydrate which will retard filtering.

There are a number of compounds on the market for which special advantages in lye

treatment are claimed. For this work, however, the lower grades of aluminum sulphate are amply efficient and cheap enough to offset any advantage of the special chemicals.

Some operators prefer to determine the amount of alkali in the lye by chemical analysis and then estimate the weight of acid to be added to bring the lye to neutral, making proper deduction for the amount of alkali neutralized by the aluminum sulphate. This, however, is unnecessary, as by means of a good neutral litmus paper (alkaline or acid will do) a careful man can bring the lye to between neutral and 0.01 % alkaline.

All lyes will contain some carbonate of soda. Carbonates in the lye have the tendency to cause foaming in the evaporator and also give misleading results with litmus. With the above in view the best procedure is as follows:-

The lye is placed in a tank which is fitted with a stirring or agitating apparatus.

With the agitator (air) in action a portion of the acid is added - enough to just take up the free caustic - then add the aluminum sulphate. After the chemical is well mixed in the lye should be alkaline. Now enough acid should be added to just carry the lye to the neutral point or perhaps to the point of acidity as indicated by the faint pink of the litmus paper. Care should be exercised to thoroughly agitate the lye during all stages of the treatment, stirring making the liquor uniformly acid or alkaline as the case may be. Agitating or stirring seems to facilitate a more readily "settable" precipitate.

All lyes will contain nitrogenous matter, the amount varying with the care used in rendering. When lyes are thus treated this is not removed, most of it appearing in the crude, increasing the figure for non-volatile organic residue. If the lye is made alkaline before evaporation this nitrogenous matter partly decomposes and gives off ammonia gas.

In the still its decomposition continues (the crude always being distilled alkaline) the ammonia gas passing out through the vacuum pump. With alkaline distillation there is no accumulation of nitrogen in the still foots when these are returned to the lyes, showing ultimate decomposition of all nitrogenous matter.

Crude lye from cottonseed soap stock contains nitrogenous acid bodies that resist this decomposition thus necessitating waste of all still residues. The same applies to crudes obtained by the autoclave or twitchell process from cottonseed soap stock and black grease.

Lyes stored free from caustic ferment, the nitrogenous matter decomposing, producing sulphides which give off hydrogen sulphide on acidifying and some glycerol is converted to trimethylene glycol.

Fermented lyes give considerable trouble in the evaporator by foaming. The sulphides

also give trouble by corroding the apparatus.
It is sometimes impossible to evaporate the
fermented lyes because of the excessive
foaming.

Glycerol Detection and Estimation.

When in a state of reasonable purity and concentration glycerol may be recognized by its physical properties. No other substance likely to be met with exhibits the combined characteristics of a dense viscous liquid of sweet taste and neutral reaction; a miscibility with water and alcohol in all proportions; volatile at a high temperature; and a burning with a blue flame when kindled, leaving no carbonaceous residue.

The most characteristic property of glycerol is its behavior when heated in a concentrated state with potassium hydrogen sulphate, whereby it is converted into acrolein ($\text{C}_3\text{H}_4\text{O}$) with the elimination of water ($\text{C}_3\text{H}_8\text{O}_3 \xrightarrow{\Delta} \text{C}_3\text{H}_4\text{O} + 2\text{H}_2\text{O}$)
The acrolein is recognizable by its extremely penetrating odor, resembling that of burning fat, and its property of causing the eyes to water. If the vapors be passed into water, the warm solution will be found to have the

properties of an aldehyde, e.g., of reducing ammoniacal silver nitrate, with the formation of a mirror of metallic silver.

The following test is recommended by Grünhut (Zeit. Anal. Chem., 1899, 37, 38,) as the best qualitative test for glycerol:-

The substance supposed to contain glycerol is mixed with twice its weight of potassium hydrogen sulphate and strongly heated until it foams; the vapors are lead into a test-tube cooled with a freezing mixture. The distillate smells strongly of acrolein if glycerol is present. To confirm, add a few drops of a mixture of solutions of three grams silver nitrate in thirty grams of ammonia sp. gr. .923 and three grams of sodium hydroxide in thirty grams of water. The silver mirror should form in the cold.

The accurate estimation of glycerol in a complex mixture with other neutral organic substances and with inorganic material, has not received a satisfactory solution under all

circumstances. The problem is complicated by the fact that solutions of glycerol can not be highly concentrated (see elsewhere) without serious loss from volatilization, and that the presence of glycerol naturally increases the solubility of many substances in aqueous and alcoholic solutions.

In general the first step in the estimation of glycerol consists in separating it from other substances with which it is mixed or combined so as to obtain it in a state of approximate purity. This can often be effected qualitatively in a very satisfactory manner, but it too often happens that the evaporations which are necessary steps in the process cause such a loss of glycerol by volatilization as to render the result of little value for quantitative purposes.

Proteins and some other foreign substances may be separated from a solution containing glycerol by adding a solution of basic lead acetate and then filtering them out of the

solution. Chlorides may be removed by the addition of some soluble silver salt such as the nitrate, or the oxide, silver chloride being precipitated and filtered from the solution.

Proteins and some other organic substances can often be removed completely by precipitating the slightly alkaline solution with zinc chloride. The precipitate is filtered off and the filtrate rendered slightly acid when further precipitation will often occur. The last traces of zinc may be removed from the solution by adding potassium ferrocyanide, which is also a very good precipitant of albumen.

At the present writing there seems to be no accurate method for the determination of glycerol of all percentages in complex mixtures. In aqueous solutions glycerol can be determined accurately by means of specific gravity and refractive index. Lenz recommends that the refractive index of glycerol solution

and pure water be observed successively. Tables in the appendix give the differences between the refractive index of water and aqueous solutions of glycerol of different concentration. The table of specific gravity of aqueous solutions is also given in the appendix.

F. Schulze (Chem. Zeit., 1905, 29, 976,) has recently made a systematic comparison of the methods in use for estimating glycerol; he gives tables showing the results obtained with fats, soaps, and various commercial glycerols. The following are his principle conclusions:-

(1) The permanganate method is considered unreliable in all cases, whether carried out by the method of Benedikt and Zsigmondy or by Herbig or Mangold's modifications.

(2) The dichromate method gives high results. Approximate values may be obtained by lowering the figures obtained by ten percent. This method is valid only in the absence of phosphoric acid.

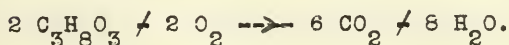
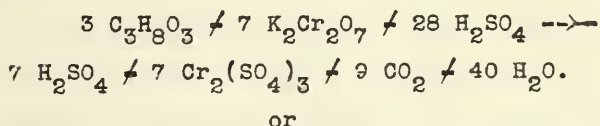
(3) Zeisel and Fanto's method is regarded as the most accurate for scientific and general purposes, but is too expensive for ordinary factory working.

(4) The acetin method failed to give concordant results. If this method is still to be employed, it is essential that the mean of several estimations be taken.

Lewkowitsch (Chemical Technology of Fats and Oils) considers that for ascertaining the proportion of glycerol in its pure dilute aqueous solution, oxidation methods are best, and that either permanganate or dichromate method gives good results in such cases. On the other hand, there is no doubt that such methods give high results with impure glycerol. In such cases the acetin method is preferred. Fanto's method is said by Lewkowitsch not to be good.

An attempt has been made to estimate the glycerol content of a solution or mixture by carbon-dioxide absorption. The method is

based upon the oxidation reaction of glycerol by dichromate in sulphuric acid solution as represented by the following equation:-



The carbon-dioxide is absorbed in potassium hydroxide (Geissler Bulb) and weighed; the carbon-dioxide is calculated to glycerol (or carbon-dioxide X .693 \rightarrow glycerol) The results upon repetition agree well. The method is easy and rapid. With pure glycerol the oxidation is quantitative. Crude glycerols must be treated to remove the impurities.

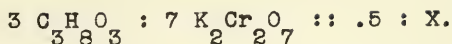
Details:-

About 5 grams of the sample is weighed (by difference) into a 250 c.c. volumetric flask, 50 c.c. of water added and the contents dissolved by shaking. A piece of blue litmus paper is dropped into the flask and

dilute sulphuric acid added until the litmus shows a faint pink. A 10 % solution of silver nitrate until all chlorine and aldehydic compounds are precipitated. Basic lead acetate is then added in slight excess to remove albumen and nitrogenous matter. Excess lead is removed by precipitating with sulphuric acid. The solution is made up to 250 c.c. and a portion filtered through a dry paper. Twenty five c.c. of the filtrate is placed in the evolution flask and 4 grams of dichromate are added. The mixture is boiled gently for one hour. The carbon-dioxide is weighed and calculated to glycerol. Carbon-dioxide times .693 gives the glycerol content. (Glycerol content) divided by (Weight of sample divided by 10) gives Percent Glycerol.

Any bubbles or froth that may be present while making up to the 250 c.c. mark may be dispelled by the addition of 2 or 3 drops of concentrated sulphuric acid.

From the proportion:-



Half a gram of pure glycerol requires 3.73 grams of potassium dichromate for complete oxidation. In operation however a slight excess is used. The dichromate solution as added to the evolution flask is made up as follows:-

4 grams of $\text{K}_2\text{Cr}_2\text{O}_7$.

25 grams of H_2O .

15 grams of H_2SO_4 .

The merits of the method may be compared and summed up as follows:-

In the titration method the dichromate solution is necessarily a somewhat stronger one, hence the measurements must be made with the greatest care, attention being paid to temperature.

In the absorption method all errors are eliminated, no attention being paid to temperature.

The titration method is open to the objection that by precipitation by lead acetate the impurities may not be perfectly removed, anything left being oxidized and counted as glycerol.

With the removal of all higher fatty acids and all resins and carbonates, as well as albuminoids, sulphides, thiocyanates, and aldehydes, (which is accomplished by the addition of basic lead acetate) the error due to oxidation is eliminated with the elimination of all carbon. The lower fatty acids such as acetic, butyric, caprylic, and formic (should they escape the metallic salts in the lye clarification) are not attacked by chromic acid. The chlorides and aldehydic compounds are removed alike with soluble silver salts in either method.

Check determinations with the absorption method agree very well with all percentages of glycerol, whereas with the other methods at hand results with low percentages are anything but concordant.

The following table gives the results of the estimation of glycerol by the absorption method on five samples and in two instances checks by the acetin method.

Sample No.	Weight of Sample	Weight of CO_2 .	Percent of Glycerol.	Weight of Sample	HCl c.c. Used.	Percent of Glycerol.
0	5.2512	.6255	82.55	1.0152	52.0	82.60
0	5.2512	.6248	82.47	1.3076	66.9	82.35
0	5.2818	.6286	82.49	1.1895	60.9	82.50
1481	5.5095	.5283	66.40	1.1076	46.0	66.35
1481	3.5437	.3378	66.10	1.0970	44.9	66.00
1481	3.5437	.3350	65.60	1.1172	45.3	65.40
1481	3.5437	.3400	66.55	.9493	39.4	66.60
1481	3.5437	.3350	65.60			
1	4.5893	.2014	30.41			
1	4.5893	.1994	30.11			
1	4.5893	.2007	30.31			
2	4.2718	.1626	26.37			
2	4.2718	.1612	26.15			
2	4.2718	.1619	26.26			
3	6.1207	.0401	4.54			
3	6.1207	.0415	4.70			

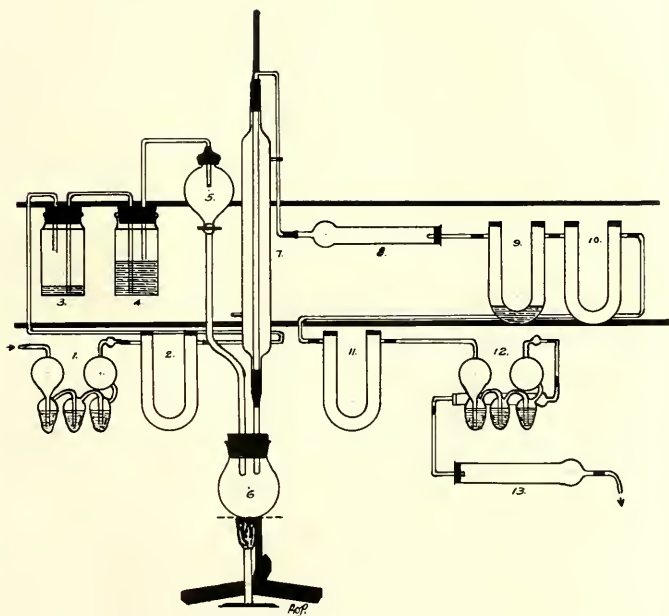
The acetin method is the one agreed upon at a conference of delegates from American, British, French, and German committees and has been confirmed by each of the above committees as giving results nearest the truth on crude glycerines in general.

The column in the above table headed "c.c. HCl used" refers to the acid equivalent of the sodium hydroxide used for the saponification of the acetin.

As 20 c.c. of strong NaOH \equiv 93.4 c.c. Std. HCl one c.c. of HCl is equivalent to .016125 grams of glycerol.

93.4 - 41.4 = 52 c.c. HCl used for saponification. (The 41.4 c.c. HCl is that used to titrate the excess of NaOH.)

The apparatus is shown in the cut. The parts, bottles, U tubes, absorption bulb, etc., are fastened to the stand (by means of wire) which consists of an upright stand and two cross rods. An aspirator is attached by means of which the evolved carbon-dioxide is drawn to the Geissler



bulb and absorbed.

The sample is put into the flask (6), the Geissler (12) having been filled with 40 % potassium hydroxide solution and weighed is put in its place and the aspirator or ordinary suction pump is started. The dichromate solution is run into the flask (6) from the dropping funnel (5) and a small flame is then applied to the flask (6). A current of (atmospheric) air enters the system (suction) at the Geissler bulb (1) where any carbon-dioxide in the air is absorbed by the 40 % potassium hydroxide therein. From the Geissler bulb the current of air goes through the soda lime U tube and then into the bottles 3 and 4 containing sulphuric acid and enters the flask (6) through the dropping funnel (5). (Any water in the air is removed by the double safety device - soda lime and sulphuric acid.) From the flask (6) the current of air plus the evolved carbon-dioxide which is forming continuously ascends through the condenser (7) to the safety tube (8) which contains moistened glass beads. These beads are inserted in the circuit as a precautionary measure for

catching any chlorine that may be present or water that has not condensed in the condenser (7).

From the tube (8) the current passes through the sulphuric acid U tube (9) and then through the calcium chloride U tube (10) where any moisture is collected. From the calcium chloride tube (8) the current passes through a second calcium chloride tube (11) and then to the Geissler (12) and small calcium chloride tube attached to the Geissler and through a calcium chloride tube to the pump, the last drying tube being a safety device to keep moisture from entering the Geissler from the pump direction.

The apparatus needs no further attention than to assure that a current of air is kept moving through the system so as to eliminate any backing up of acid in bottles 3 and 4.

Properties.

Glycerol, or "chemically pure" glycerine is a colorless, odorless, viscid liquid, having a sweet taste. It is optically inactive and is neutral to indicators. On exposure to cold for a prolonged time it crystallizes in rhombic crystals which melt at 20° centigrade. With the aid of a few crystals large quantities of glycerol can be easily converted into a crystalline mass at 0° centigrade.

Glycerol is oily to the touch and produces on the skin, especially the mucuous membranes, the sensation of heat, due to its power of absorbing moisture from the tissues. The water absorbing power of glycerol amounts to 50 % of its own weight.

At ordinary temperatures glycerol does not volatilize; at the boiling point of water, however, appreciable quantities escape as vapor. Glycerol boils under 760 m.m. at 290° C with a slight decomposition. At pressures under 12 m.m. it distills unchanged. The specific

gravity as given by the most reliable observers is:-

$$d_{\frac{15^{\circ}}{15^{\circ}}} C = 1.26468, \quad d_{\frac{17.5^{\circ}}{17.5^{\circ}}} C = 1.2620$$

The following table computed by Richardson and taken from Lewkowitsch. Vol. 1, Fifth Ed. contains the most reliable observations of boiling points under reduced pressures.

Pressure In Millimeters	Boiling Points In Degrees Centigrade.
385.33	269.4
347.10	257.3
231.87	250.3
201.23	241.8
100.81	220.3
50.00	210.0
45.61	201.3
30.00	191.8
20.46	183.3
20.00	182.0
15.00	176.0
10.00	167.2

Pressure In Millimeters	Boiling Points In Degrees Centigrade
6.53	161.3
5.00	156.5
.24	118.5
.056	115.166

Glycerol is miscible with water in all proportions. On mixing water with glycerol a contraction of volume and a rise in temperature takes place. The greatest increase - viz 5°C is observed when 58 parts of glycerol (by weight) are mixed with 42 parts of water. The greatest contraction is 7.1 %. (Gerlach)

The vapor pressure of a dilute solution of glycerol rises with the rise of temperature of a boiling solution, so that considerable amounts of glycerol volatilize with water vapor. Theoretically a mixture of saturated water and glycerol vapors under the ordinary atmospheric pressure, cannot contain more than from 0.2 to 0.3 % glycerol, provided that the two vapors are not miscible. Since, however,

glycerol and water are miscible in all proportions, the composition of the escaping vapors cannot be calculated according to Dalton's well known law, but must be derived from actual observations. Gerlach determined, with the aid of a vaporimeter, in which the pressure of the vapor was measured by a column of mercury, the vapor pressures as given in the appendix.

From the table an approximate measure can be derived as to the losses that may be incurred on evaporating dilute solutions of glycerol.

Experiments showed that up to a concentration of about 50 % no glycerol escapes with the water vapors, even if the dilute solutions be kept boiling for some little time. At a concentration of about 70 % traces of glycerol escape from the boiling solution. (Hehner.) The boiling point of such a solution is 113.6° C. (See table.) Above this concentration notable amounts of

glycerol escape.

A table in the appendix gives the specific gravity of glycerol solutions in water. (It is with the aid of some reliable table that the strength of chemically pure glycerol is most accurately determined. Of those published the one by Gerlach is the most accurate.)

The coefficients of expansion of glycerine vary with the different authors. Hehner states that it amounts to $.00058^{\circ}$ C for each degree centigrade in the neighborhood of 15.5° C. According to Gerlach's observations the value of the coefficient varies with the temperatures as follows:-

Temperature Degrees Centigrade.	Coefficient.
5.0	.00057
12.5	.000587
20.0	.0006
30.0	.000619

Investigation by Comey and Backus gives the following figures;

Temperature Degrees Centigrade	Coefficient
20.0	.000612
25.0	.000617
30.0	.000622

Glycerol is miscible with alcohol in all proportions. It dissolves easily in a mixture of alcohol and ether but is sparingly soluble in ether alone, one part of glycerol, sp. gr. 1.23, requiring about 500 parts of ether. Glycerol is soluble in acetone. Nine parts of glycerol are soluble in 100 parts of ethyl acetate. Glycerol is insoluble in chloroform, petroleum ether, carbon bisulphide, and benzene; it is also insoluble in oils and fats. (Lewkowitsch.)

Glycerol has powerful solvent properties; it combines in this respect the properties of water and alcohol; many substances are more easily dissolved by it than either water or

alcohol. The following table of solubilities will serve to illustrate this:-

100 parts of glycerol dissolve at 15° C :-

98	"	"	crystal sodium carbonate.
60	"	"	borax.
50.5	"	"	potassium arsenate.
50	"	"	sodium "
50	"	"	zinc chloride.
48.8	"	"	tannic acid.
40	"	"	alum.
40	"	"	zinc iodide.
40	"	"	potassium iodide.
35.2	"	"	zinc sulphate.
32	"	"	potassium cyanide.
30	"	"	copper sulphate.
25	"	"	ferrous sulphate.
25	"	"	potassium bromide.
20	"	"	lead acetate.
20	"	"	ammonium carbonate.
20	"	"	arsenious acid.
20	"	"	ammonium chloride.
15	"	"	oxalic acid.

11	parts	of	boric acid.
10	"	"	barium chloride.
10	"	"	copper acetate.
10	"	"	benzoic acid.
8	"	"	sodium bicarbonate.
7.5	"	"	mercury bichloride.
5	"	"	potassium chloride.
3.7	"	"	potassium chlorate.
1.9	"	"	iodine.
About 1	"	"	calcium sulphate.
"	.25"	"	phosphorus.
"	.01"	"	sulphur.

An aqueous solution of glycerol, sp. gr. 1.114, dissolves 0.957 % of calcium sulphate. Metallic soaps (which are insoluble in water) are to some extent dissolved thus:-

100 parts of glycerol, sp. gr. 1.114, dissolve:-

1.18	parts	of	calcium oleate.
.94	"	"	magnesium oleate.
.71	"	"	iron oleate.

The great solubility in glycerol of zinc

sulphate, also of nickel, cobalt, and copper sulphates is explained by the fact that those salts combine with three molecules of glycerol to form complex compounds of the general formula $(M \cdot 3 C_3H_8O_3)SO_4 \cdot H_2O$. For these compounds Grün and Bockish proposed the name glycerinates, to distinguish them from the metallic glycerides (glyceroxides) mentioned above. The glycerinates are precipitated from their aqueous solutions by alcohol as amorphuous substances.

It has been pointed out that glycerol is able to form mono-acid and di-acid esters. These are usually described as monoglycerides or diglycerides. They do not occur in nature.

The most important esters of glycerol are those resulting from the combination of glycerol with fatty acids.

Glycerol also forms esters with inorganic acids, the most important being those formed with carbonic, sulphuric, nitric, phosphoric, boric, and arsenious acids. Some of these

later esters have acquired great importance in the arts and in pharmacy.

A detailed account of the "Metallic Glycer-oxides, Metallic Glycerinates, and Esters" may be found in Vol I of Lewkowitsch, Fifth Ed., Pages 251 to 262.

Glycerol dissolves caustic alkalies, alkaline earths, and lead oxide to form chemical compounds. (Chevreul.) Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the earths escaping precipitation. In the presence of caustic alkalies, glycerol also dissolves ferric oxide, cupric oxide, and bismuth oxide, owing to the formation of soluble metallic glyceroxides. However the following oxides are reduced to metals when heated with alkaline glycerol solution. (Bullenheimer.)

Silver Oxide	(Ag_2O)
Gold Oxide	(Au_2O_3)
Mercury Oxide	(HgO)

Rhodium Oxide (RdO_2)

Palladium Oxide (PdO)

Platinum Oxide (PtO_2)

Freshly precipitated cero-hydroxide is very easily soluble in glycerol; this solution is readily dissociated by addition of water. The solution becomes turbid very gradually and finally the hydroxide is precipitated in a gelatinous form. (A. Muller.) Turbidity of the perfectly clear solution sets in more rapidly, the more dilute the original solution was.

A P P E N D I X .

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Boiling Points at Reduced Pressures.

(As compiled by Gerlach)

Glycerol Percent.	Water Percent	Boiling Point 760 mm Pressure	Vapor Pressure At 100° C
100	0	290	64
99	1	239	87
98	2	208	107
97	3	188	126
96	4	175	144
95	5	164	162
94	6	156	180
93	7	150	198
92	8	145	215
91	9	141	231
90	10	138	247
89	11	135	263
88	12	132.5	279
87	13	130.5	295
86	14	129	311
85	15	127.5	326
84	16	126	340
83	17	124.5	355

Boiling Points at Reduced Pressures.

Glycerol Percent.	Water Percent	Boiling Point 760 mm Pressure	Vapor Pressure At 100° C.
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118.2	430
76	24	117.4	440
75	25	116.7	450
74	26	116	460
73	27	115.4	470
72	28	114.8	480
71	29	114.2	489
70	30	113.6	496
65	35	111.3	553
60	40	109	565
55	45	107.5	593
50	50	106	618
45	55	105	639

Boiling Points at Reduced Pressures.

Glycerol Percent.	Water Percent	Boiling Point 760 mm Pressure	Vapor Pressure At 100° C.
40	60	104	657
35	65	103.4	675
30	70	102.8	690
25	75	102.3	704
20	80	101.8	717
10	90	100.9	740
0	100	100	760

Specific Gravity of Aqueous Solutions of Glycerol.

(As compiled by Gerlach)

Glycerol	Sp.Gr.At 15°C	Sp.Gr.At 20°C	Sp.Gr.
Percent	Water At 15°C=1	Water At 20°C=1	At 15°C
0	1.0000	1.0000	1.0000
1			1.0024
2			1.0048
3			1.0072
4			1.0096
5			1.0120
6			1.0144
7			1.0168
8			1.0192
9			1.0216
10	1.0245	1.0235	1.0240
11			1.0265
12			1.0290
13			1.0315
14			1.0340
15			1.0365
16			1.0390

Glycerol.	Sp.Gr.At 15°C	Sp.Gr.At 20°C	Sp.Gr.
Percent	Water At 15°C=1	Water At 20°C=1	At 15°C

17			1.0415
18			1.0440
19			1.0465
20	1.0490	1.0480	1.0490
21			1.0516
22			1.0542
23			1.0568
24			1.0594
25	1.0620	1.0610	1.0620
26			1.0646
27			1.0672
28			1.0698
29			1.0724
30	1.0750	1.0740	1.0750
31			1.0777
32			1.0804
33			1.0831
34			1.0858
35	1.0885	1.0875	1.0885
36			1.0912

Glycerol	Sp.Gr.At 15°C	Sp.Gr.At 20°C	Sp.Gr.
Percent. Water At 15°C=1	Water At 20°C=1	At 15°C.	
37			1.0939
38			1.0966
39			1.0993
40	1.1020	1.1010	1.1020
41			1.1047
42			1.1074
43			1.1101
44			1.1128
45	1.1155	1.1145	1.1155
46			1.1182
47			1.1209
48			1.1236
49			1.1263
50	1.1294	1.1280	1.1290
51			1.1318
52			1.1346
53			1.1374
54			1.1402
55	1.1430	1.1415	1.1430
56			1.1458

Glycerol	Sp.Gr.At 15°C	Sp.Gr.At 20°C	Sp.Gr.
Percent. Water At 15°C=1	Water At 15°C=1	Water At 20°C=1	At 15°C.

57			1.1486
58			1.1514
59			1.1542
60	1.1570	1.1550	1.1570
61			1.1599
62			1.1628
63			1.1657
64			1.1686
65	1.1711	1.1685	1.1715
66			1.1743
67			1.1771
68			1.1799
69			1.1827
70	1.1850	1.1820	1.1855
71	1.1878	1.1847	1.1882
72	1.1906	1.1874	1.1909
73	1.1934	1.1901	1.1936
74	1.1962	1.1928	1.1963
75	1.1990	1.1955	1.1990
76	1.2018	1.1982	1.2017

Glycerol Percent.	Sp.Gr.At 15°C Water At 15°C=1	Sp.Gr.At 20°C Water At 20°C=1	Sp.Gr. At 15°C
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77	1.2046	1.2089	1.2044
78	1.2074	1.2036	1.2071
79	1.2102	1.2063	1.2098
80	1.2130	1.2090	1.2125
81	1.2157	1.2117	1.2152
82	1.2184	1.2144	1.2179
83	1.2211	1.2171	1.2206
84	1.2238	1.2198	1.2233
85	1.2265	1.2225	1.2260
86	1.2292	1.2252	1.2287
87	1.2319	1.2279	1.2314
88	1.2346	1.2306	1.2341
89	1.2373	1.2333	1.2368
90	1.2400	1.2360	1.2395
91	1.2425	1.2386	1.2421
92	1.2451	1.2412	1.2447
93	1.2476	1.2438	1.2473
94	1.2501	1.2464	1.2499
95	1.2526	1.2490	1.2525
96	1.2552	1.2516	1.2550

Glycerol	Sp.Gr.At 15°C	Sp.Gr.At 20°C	Sp.Gr.
Percent. Water At 15°C=1	Water At 15°C=1	Water At 20°C=1	At 15°C.

97	1.2557	1.2542	1.2575
98	1.2602	1.2568	1.2600
99	1.2608	1.2594	1.2625
100	1.2653	1.2620	1.2650

Tables of Refractive Index, n_d at 12.5 to
12.8°C of Aqueous Solutions of Glycerol. (Lenz)

Also Differences between Refractive Indices
of Aqueous Solutions of Glycerol and Pure Water.

Percent Glycerol.	n_d .	Differences.
100	1.4758	.1424
99	1.4744	.1410
98	1.4729	.1395
97	1.4715	.1381
96	1.4700	.1366
95	1.4686	.1352
94	1.4671	.1337
93	1.4657	.1323
92	1.4642	.1308
91	1.4628	.1294
90	1.4613	.1279
89	1.4598	.1264
88	1.4584	.1250
87	1.4569	.1235
86	1.4555	.1221
85	1.4540	.1206

Percent Glycerol.	Nd.	Differences.
84	1.4525	.1191
83	1.4511	.1177
82	1.4496	.1162
81	1.4482	.1148
80	1.4467	.1133
79	1.4453	.1119
78	1.4438	.1104
77	1.4424	.1090
76	1.4409	.1075
75	1.4395	.1061
74	1.4380	.1046
73	1.4366	.1032
72	1.4352	.1018
71	1.4337	.1003
70	1.4321	.0987
69	1.4304	.0970
68	1.4286	.0952
67	1.4267	.0933
66	1.4249	.0915
65	1.4231	.0897
64	1.4213	.0889

Percent Glycerol.	Nd.	Differences.
63	1.4195	.0861
62	1.4176	.0842
61	1.4158	.0824
60	1.4140	.0806
59	1.4126	.0792
58	1.4114	.0780
57	1.4102	.0768
56	1.4091	.0757
55	1.4079	.0745
54	1.4065	.0731
53	1.4051	.0717
52	1.4036	.0702
51	1.4022	.0688
50	1.4007	.0663
49	1.3993	.0659
48	1.3979	.0645
47	1.3964	.0630
46	1.3958	.0616
45	1.3935	.0601
44	1.3921	.0587
43	1.3906	.0572

Percent Glycerol.	Nd.	Differences.
42	1.3890	.0556
41	1.3875	.0541
40	1.3860	.0526
39	1.3844	.0510
38	1.3829	.0495
37	1.3813	.0479
36	1.3798	.0464
35	1.3785	.0451
34	1.3772	.0438
33	1.3758	.0424
32	1.3745	.0411
31	1.3732	.0398
30	1.3719	.0385
29	1.3706	.0372
28	1.3692	.0358
27	1.3679	.0345
26	1.3666	.0332
25	1.3652	.0318
24	1.3639	.0315
23	1.3626	.0302

Percent Glycerol.	Nd.	Differences.
22	1.3612	.0288
21	1.3599	.0275
20	1.3585	.0261
19	1.3572	.0238
18	1.3559	.0225
17	1.3546	.0212
16	1.3533	.0199
15	1.3520	.0186
14	1.3507	.0173
13	1.3494	.0160
12	1.3480	.0146
11	1.3467	.0133
10	1.3454	.0120
9	1.3442	.0108
8	1.3430	.0096
7	1.3417	.0083
6	1.3405	.0071
5	1.3392	.0058
4	1.3380	.0046
3	1.3367	.0033
2	1.3355	.0021
1	1.3343	.0008
0	1.3330	

